

BE IT KNOWN, that we, DENNIS J. O'REAR, residing in the City of Petaluma, County of Sonoma, State of California; and CHARLES L. KIBBY, residing in the City of Benicia, County of Solano, State of California; have invented new and useful improvements in:

**CONTROL OF CO₂ EMISSIONS FROM A FISCHER-TROPSCH
FACILITY BY USE OF MULTIPLE REACTORS**

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CONTROL OF CO₂ EMISSIONS FROM A
FISCHER-TROPSCH FACILITY BY USE OF MULTIPLE REACTORS

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FIELD OF THE INVENTION

The present invention is directed to controlling CO₂ emissions from Fischer-Tropsch facilities. In particular, the present invention is directed to controlling CO₂ emissions from a Fischer-Tropsch facility by using multiple reactors.

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BACKGROUND OF THE INVENTION

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The conversion of natural gas assets into more valuable products, including combustible liquid fuels, is desired to more effectively utilize these natural gas assets. The conversion of natural gas to more valuable products generally involves syngas generation. Syngas generation involves converting natural gas, which is mostly methane, to synthesis or syngas gas, which is a mixture of carbon monoxide and hydrogen. Syngas may be used as a feedstock for producing a wide range of products, including combustible liquid fuels, methanol, acetic acid, dimethyl ether, oxo alcohols, and isocyanates.

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There are two main approaches to convert remote natural gas assets into conventional transportation fuels and lubricants using syngas. Natural gas may be converted into syngas followed by a Fischer-Tropsch process, or natural gas may be converted into syngas followed by methanol synthesis, which is followed by a methanol to gas process (MTG) to convert methanol into highly aromatic gasoline. The syngas generation is the most costly step of these processes. A critical feature of these processes is producing syngas with a desired H₂/CO ratio to optimize formation of the desired products and to avoid problems in the syngas formation step. Unless otherwise stated, syngas ratios (and percentage compositions) as described herein are in terms of molar ratios (and molar percentages).

Syngas can be generated from three major chemical reactions. The first involves steam reforming of methane. The ratio of hydrogen to carbon monoxide, which is formed

from this process, is typically approximately 3.0. A second process for syngas generation involves dry reforming of methane or the reaction between carbon dioxide and methane. An attractive feature of this method is that carbon dioxide is converted into syngas; however, this method has problems with rapid carbon deposition. The carbon deposition or coke forming reaction is a separate reaction from the one that generates the syngas and occurs subsequent to the syngas formation reactor. However, the reaction of methane in dry reforming is slow enough that long residence times are required for high conversion rates and these long residence times lead to coke formation. The ratio of hydrogen to carbon monoxide, which is formed from this process, is typically approximately 1.0. A third process for synthesis gas generation involves partial oxidation of methane using oxygen. The ratio of hydrogen to carbon monoxide, which is formed from this process, is typically approximately 2.0. However, in commercial practice, some amount of steam is typically added to a partial oxidation reformer in order to control carbon formation and the addition of steam tends to increase the H_2/CO ratio above 2.0.

It is possible to produce syngas with a H_2/CO ratio that is above the ratio ideally desired for the process in which the syngas is to be used, and then to remove excess hydrogen to adjust the ratio to the desired value. However, the H_2 removal process employs expensive H_2 separation systems that tend to foul and decline in performance with use.

The Fischer-Tropsch and MTG processes both have advantages and disadvantages. For instance, the Fischer-Tropsch process has the advantage of forming products that are highly paraffinic. Highly paraffinic products are desirable because they exhibit excellent combustion and lubricating properties. Unfortunately, a disadvantage of the Fischer-Tropsch process is that the Fischer-Tropsch process emits relatively large amounts of CO_2 during the conversion of natural gas assets into saleable products. An advantage of the MTG process is that the MTG process produces highly aromatic gasoline and LPG fractions (e.g., propane and butane). However, while highly aromatic gasoline produced by the MTG process is generally suitable for use in conventional gasoline engines, highly aromatic MTG gasoline may be prone to form durene and other polymethyl aromatics

having low crystallization temperatures that form solids upon standing. In addition, the MTG process is more expensive than the Fischer-Tropsch process and the products produced by the MTG process cannot be used for lubricants, diesel engine fuels or jet turbine fuels. Furthermore, like the Fischer-Tropsch process, the MTG process also
5 generates CO₂.

It is known to use multiple Fischer-Tropsch reactors for various purposes. For instance, U.S. Patent No. 6,169,120, to Beer of Syntroleum, discloses a two-stage Fischer-Tropsch process employing intermediate H₂O removal. The process of Beer is intended to be used to process syngas produced from air that will contain appreciable amounts of
10 nitrogen.

U.S. Patent No. 4,279,830, to Haag et al. of Mobil, discloses a zeolite-containing catalyst used to maintain a syngas composition so that a H₂:CO ratio is in a range of about 0.5 to about 1.0. Haag explains that this range is appropriate for Fe-based FT catalysts, but is not suitable for Co-based catalysts. A second FT catalyst contains Fe but does not
15 contain a zeolite. This catalyst makes a minimal change in the H₂:CO ratio. *Haag* also explains that operating within a selective range of process conditions provides an improved process for upgrading the total effluent from a Fischer-Tropsch operation.

U.S. Patent No. 4,624, 968, to Kim et al. of Exxon, discloses a two-stage Fischer-Tropsch process using specific catalysts intended for olefin synthesis and conversion.

20 WO/0063141, to Clark et al. of Reema International Corp., discloses a Fischer-Tropsch process for synthesizing hydrocarbons that includes multiple Fischer-Tropsch reactor stages arranged in series. The process of Clark provides very low CO conversion per Fischer-Tropsch reactor stage and employs intermediate removal of water between reactor stages. In one embodiment, the process of Clark uses an iron-based catalyst. In a
25 preferred embodiment, CO₂ is recycled from the last reactor in a series of Fischer-Tropsch reactors to the syngas generator.

EP 0679620 A2, to Long of Exxon, discloses a high conversion hydrocarbon synthesis achieved by reacting H₂ and CO in a first stage(s) in the presence of a non-

shifting catalyst. The process further includes separating liquid products and reacting the remaining gas streams in the presence of shifting catalysts.

Additionally, various technologies have been used for the conversion of CO₂. For instance, "Can Carbon Dioxide be Reduced to High Molecular Weight in Fischer-Tropsch Products?," In re Puskas, ACS 213 National Meeting (San Francisco 4/13-17/97) ACS Division of Fuel Chemistry Preprints, V.42, N.2, 680-86 (1997), discloses that CO₂ can be converted into hydrocarbonaceous products of similar structure and composition as obtained with CO. Also, "Kinetics of CO₂ hydrogenation on a K-promoted Fe Catalyst," Thomas Riedel and Georg Schaub, Industrial and Engineering Chemistry Research, 40/5 1355-1363, discloses that CO₂ can be converted into hydrocarbonaceous products of similar structure and composition as obtained with CO. Riedel and Schaub discloses that preferred operating temperatures are below 360°C to prevent rapid carbon deposition on the catalyst.

Similarly, "Iron Catalyzed CO₂ Hydrogenation to Liquid Hydrocarbons," Fourth International Carbon Dioxide Utilization Conference (Kyoto, Japan 9/7-11/97) Studies in Surface Science and Catalysis, V114, 339-44 (1998), discloses that many catalysts useful in Fischer-Tropsch synthesis can also catalyze CO₂ hydrogenation to hydrocarbons.

Although multiple Fischer-Tropsch reactors have been used, an integrated system employing multiple Fischer-Tropsch reactors wherein hydrocarbonaceous products from different stages are blended has not been utilized to reduce CO₂ emissions.

As a result, there is an urgent need for a process that can reduce CO₂ emissions from syngas conversion processes while still being able to generate desired hydrocarbonaceous products.

SUMMARY OF THE INVENTION

The present invention satisfies the above objectives by providing a process that uses multiple reactors to control CO₂ emissions generated from a syngas conversion process. By using multiple reactors, the present invention avoids the need for costly CO₂ isolation processes.

The process according to the present invention, for the conversion of syngas using multiple Fischer-Tropsch reactors, includes reacting at least a portion of a first syngas, comprising at least about 2 vol% CO₂, in a first Fischer-Tropsch reactor to form a first hydrocarbonaceous product and a second syngas comprising at least about 2 vol% CO₂.
5 The process also includes mixing the second syngas with a H₂-containing stream to form an adjusted syngas. The process further includes reacting at least a portion of the adjusted syngas in a second Fischer-Tropsch reactor to form a second hydrocarbonaceous product and a third syngas comprising a reduced amount of CO₂ than was present in the adjusted syngas. Finally, the process includes blending at least a portion of the first and second
10 hydrocarbonaceous products to obtain a blended hydrocarbonaceous product.

According to another aspect of the present invention, the process for the conversion of syngas using multiple Fischer-Tropsch reactors includes forming a first syngas comprising at least about 2 vol% CO₂. The process also includes reacting at least a portion of the first syngas in a first Fischer-Tropsch reactor to form a first hydrocarbonaceous
15 product and a second syngas comprising at least about 2 vol% CO₂. The process further includes mixing the second syngas with a H₂-containing stream to obtain an adjusted syngas having a molar ratio of H₂:(CO+CO₂) of at least about 1.0, and preferably between about 1.0 and about 8.0. The process also includes reacting at least a portion of the adjusted syngas in a second Fischer-Tropsch reactor to form a second hydrocarbonaceous
20 product and a third syngas comprising a reduced amount of CO₂ than was present in the adjusted syngas. Finally, the process includes blending at least a portion of the first and second hydrocarbonaceous products. In a preferred embodiment, the process can further include converting at least a portion of the blended hydrocarbonaceous product into at least one product selected from the group consisting of jet fuel, diesel fuel, lubricant base oil,
25 naphtha, and combinations thereof.

In yet another embodiment of the present invention, the process includes reacting at least a portion of a blended syngas comprising a first syngas and containing at least about 2 vol% CO₂ in a first Fischer-Tropsch reactor to form a first hydrocarbonaceous product and a second syngas comprising at least about 2 vol% CO₂. The process also includes mixing

the second syngas with a H_2 -containing stream to form an adjusted syngas. The process further includes reacting at least a portion of the adjusted syngas in a second Fischer-Tropsch reactor to form a second hydrocarbonaceous product and a third syngas comprising a reduced amount of CO_2 than was present in the adjusted syngas. The process
5 also includes blending at least a portion of the first and second hydrocarbonaceous products to obtain a blended hydrocarbonaceous product. Finally, the process includes recycling at least a portion of the third syngas to be mixed with the first syngas to form the blended syngas:

According to a further aspect of the present invention, a Gas-to-Liquids facility
10 includes a first Fischer-Tropsch reactor that reacts at least a portion of a first syngas, comprising at least about 2 vol% CO_2 , to form a first hydrocarbonaceous product and a second syngas comprising at least about 2 vol% CO_2 . The facility further includes a hydrogen source that provides hydrogen that mixes with the second syngas to form an adjusted syngas. The facility also includes a second Fischer-Tropsch reactor that reacts at
15 least a portion of the adjusted syngas to form a second hydrocarbonaceous product and a third syngas comprising a reduced amount of CO_2 than was present in the adjusted syngas. Finally, the facility includes a blender that blends at least a portion of the first and second hydrocarbonaceous products to produce a blended hydrocarbonaceous product.

The process of the present invention, through the use of its multiple reactors,
20 thereby realizes an important advantage in that it substantially minimizes CO_2 emissions generated from a syngas conversion process without having to employ costly CO_2 isolation processes such as, for example, CO_2 compression, liquefaction or solidification to isolate CO_2 from CH_4 -containing gases. In addition, by blending at least a portion of the first and second hydrocarbonaceous products, the present invention can produce a blended
25 hydrocarbonaceous product that substantially minimizes or eliminates the need for additional distillation and/or upgrading. Further, when at least a portion of the third syngas is recycled, the present invention provides a blended syngas that becomes enriched in methane as CO_2 is removed. The result is a process and facility that can operate more efficiently and economically in the production of hydrocarbonaceous products.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic view of a conventional Fischer-Tropsch synthesis.

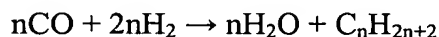
Figure 2 is a schematic view of an exemplary embodiment of a syngas conversion
5 process of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention, CO₂ emissions from a syngas conversion process are
effectively reduced by using multiple reactors.

10 One such syngas conversion process is a Fischer-Tropsch process. Catalysts and
conditions for performing Fischer-Tropsch reactions are well known to those of skill in the
art, and are described, for example, in EP 0 921 184A1, the disclosure of which is hereby
incorporated by reference in its entirety. A schematic of a conventional Fischer-Tropsch
process is shown in Figure 1.

15 The Fischer-Tropsch process can be understood by examining the stoichiometry of
the reaction that occurs during a Fischer-Tropsch process. For example, during Fischer-
Tropsch processing, synthesis gas (i.e., a mixture including carbon monoxide and
hydrogen), is generated, typically from at least one of three basic reactions. Typical
Fischer-Tropsch reaction products include paraffins and olefins, generally represented by
20 the formula C_nH_{2n+2}. While this formula accurately defines mono-olefin products, it only
approximately defines C₅₊ paraffin products. The value of n (i.e., the average carbon
number of the product) is determined by reaction conditions including, but not limited to,
temperature, pressure, space rate, catalyst type and synthesis gas composition. The desired
net synthesis gas stoichiometry for a Fischer-Tropsch reaction is independent of the
25 average carbon number (n) of the product and is about 2.0, as determined by the following
reaction equation:



where C_nH_{2n+2} represents typical Fischer-Tropsch reaction products such as, for example,
olefins and paraffins. The amount of by-product water produced by the reaction is

significant. For instance, when converting the molar ratios to weight ratios, one can see that the relative weight percentages of water to CH₂ hydrocarbons is 56%/44%.

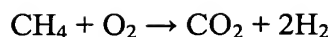
The three general reactions that produce synthesis gas from methane are as follows:

1. steam reforming of methane: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$;
- 5 2. dry reforming, or reaction between CO₂ and methane: $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$; and
3. partial oxidation using oxygen: $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$.

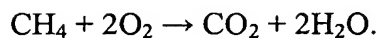
Although the above general reactions are the basic reactions used to produce
 10 synthesis gas, the ratio of hydrogen to carbon monoxide produced by the above reactions is not always adequate for the desired Fischer-Tropsch conversion ratio of 2.0. For example, in the steam reforming reaction, the resulting ratio of hydrogen to carbon monoxide is 3.0, which is higher than the desired hydrogen to carbon monoxide ratio of 2.0 for a Fischer-Tropsch conversion. Similarly, in the dry reforming reaction, the resulting hydrogen to
 15 carbon monoxide ratio is 1.0, which is lower than the desired hydrogen to carbon monoxide ratio of 2.0. In addition to exhibiting a hydrogen to carbon monoxide ratio that is lower than the desired ratio for a Fischer-Tropsch conversion, the above dry reforming reaction also suffers from problems associated with rapid carbon deposition. Finally, because the above partial oxidation reaction provides a hydrogen to carbon monoxide ratio
 20 of 2.0, the partial oxidation reaction is the preferred reaction for Fischer-Tropsch conversions.

In commercial practice, an amount of steam added to a partial oxidation reformer can control carbon formation. Likewise, certain amounts of CO₂ can be tolerated in the feed. Thus, even though partial oxidation is the preferred reaction for Fischer-Tropsch
 25 conversions, all of the above reactions can occur, to some extent, in an oxidation reformer.

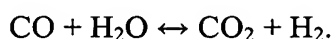
During partial oxidation, CO₂ forms because the reaction is not perfectly selective. That is, some amount of methane in the reaction will react with oxygen to form CO₂ by complete combustion. The reaction of methane with oxygen to form CO₂ is generally represented by the following reactions:



and



Furthermore, steam added to the reformer to control coking, or steam produced during the Fischer-Tropsch reaction can react with CO to form CO₂ in a water gas shift reaction at various points in the process including in the syngas generator, in the syngas shift unit, and in the Fischer-Tropsch reactor. The reaction is represented by the following general reaction:



In addition, light by-product gases, including C₁-C₄ hydrocarbons, are frequently used as fuel in furnaces. These fuels often include CO₂ from a GTL facility along with some unreacted CO. Moreover, during operation, a furnace provides heat that can contribute to the generation of substantial amounts of CO₂.

Thus, invariably a significant amount of CO₂ is formed during the conversion of methane into transportation fuels and lubricants by the Fischer-Tropsch process. The CO₂ produced during the Fischer-Tropsch process exits the Fischer-Tropsch/GTL process in a tail gas exiting the Fischer-Tropsch unit. Tail gases exiting a Fischer-Tropsch/GTL process comprise any gases that remain unconsumed by the Fischer-Tropsch process.

The overall proportion of carbon in methane that is converted to heavier hydrocarbon products has been estimated to be as high as about 68%. Thus, the remaining 32% can form significant amounts of CO₂. These estimates of carbon efficiency are provided, for example, by Bechtel Corporation for a GTL complex using cryogenic air separation, an autothermal reformer, a slurry bed Fischer-Tropsch unit and a hydrocracker for conversion of heavy wax into saleable products. See "CO₂ Abatement in GTL Plant: Fischer-Tropsch Synthesis," Report # PH3/15, November 2000, published by IEA Greenhouse Gas R&D Programme, the disclosure of which is hereby incorporated by reference in its entirety. Additionally, although the above estimates are provided for a specific GTL complex, it is believed that similar carbon efficiencies and CO₂ emissions would be produced by GTL processes employing alternative technologies.

The above equations represent general stoichiometric equations, and do not reflect an optimum synthesis gas composition for the kinetics or selectivity of a Fischer-Tropsch reaction. Moreover, depending on the nature of the Fischer-Tropsch catalyst, synthesis gas ratios other than 2.0, typically less than 2.0, are used to prepare the feed to a Fischer-Tropsch unit. However, because Fischer-Tropsch units typically produce products exhibiting a hydrogen to carbon ratio of about 2.0, the limiting reagent, typically H_2 , is consumed first. The extra reagent, typically CO, is then recycled back to the Fischer-Tropsch unit for further conversion. Synthesis gas compositions having hydrogen to carbon ratios other than 2.0 are typically generated by recycling unused reagents.

In order to control the reaction, Fischer-Tropsch processes often operate at less than 100% conversion of the CO in the syngas. Typical conversion values are between about 40% and about 70% per pass. In Fischer-Tropsch processes that use O_2 (typically 99.5% purity), rather than air, unreacted syngas is recycled to the Fischer-Tropsch process. From the standpoint of economics and operational efficiency, preferred Fischer-Tropsch processes use a catalyst in a slurry bed. Also, from a practicality standpoint, the most common catalyst for use in slurry bed units contains cobalt. Cobalt does not promote the water-gas shift reaction or the reverse of the reaction. In these units, CO_2 is, for the most part, an inert gas. As syngas is recycled to the Fischer-Tropsch unit, its concentration builds up. As a result, the concentration of the reactive syngas components ($CO + H_2$) is effectively lowered, thereby reducing the rate of reaction. To compensate for the lower partial pressures of the reactive components, the pressure of the Fischer-Tropsch reactor is increased. During this recycle operation, a small amount of CO_2 in the initial syngas (typically about 5 vol% but always at least about 2 vol%) increases to much larger values (typically about 40 vol%).

In commercial practice, a portion of the CO_2 -enriched recycled gas is typically recycled to a syngas generator where it promotes a dry reforming reaction and reduces the ratio of $H_2:CO$ in the syngas to a desired level. However, much more CO_2 is produced than can be consumed in the syngas generator. Thus, excess CO_2 -enriched recycled gas is

purged from the process and used as a low-energy content fuel. This low-energy-content fuel is a significant source of CO₂ emissions generated from syngas conversion processes.

In preferred embodiments of the present invention, a first syngas, preferably containing at least about 2 vol% CO₂, is reacted in a first Fischer-Tropsch reactor to
5 produce a first hydrocarbonaceous product and a by-product of unreacted syngas having an increased CO₂ content. The by-product of unreacted syngas constitutes a second syngas. The second syngas may be mixed with a H₂-containing stream to form an adjusted syngas. Next, the second or adjusted syngas is reacted in a second Fischer-Tropsch reactor to produce additional hydrocarbonaceous product and a third syngas comprising a reduced
10 amount of CO₂ than was present in the feed to the second Fischer-Tropsch reactor. Optionally, a H₂-containing stream may be added to the Fischer-Tropsch reactor if the second syngas stream is not mixed with a H₂-containing stream to form an adjusted syngas prior to entering the reactor. Further, at least a portion of the third syngas can be recycled to the first Fischer-Tropsch reactor for additional processing. That is, at least a portion of
15 the third synthesis gas can be recycled to mix with the first syngas and optionally a H₂-containing stream to produce a blended syngas at least one of before, during or after entering the first Fischer-Tropsch reactor. Because the resulting blended syngas is rich in methane, the blended syngas is not only easier to burn, but also provides greater process control. Additionally, the hydrocarbonaceous products produced by the first two Fischer-
20 Tropsch reactors can be combined to form a blended hydrocarbonaceous product. By blending the hydrocarbonaceous products to obtain a blended hydrocarbonaceous product, the present invention can substantially minimize or eliminate the need for further distillation and/or upgrading. As a result, the present invention is less costly and more efficient than conventional hydrocarbon product syntheses.

25 At least a portion of the blended hydrocarbonaceous product may be converted into more valuable products including jet fuel, diesel fuel, lubricant base oil, and naphtha. Furthermore, it may be desirable to combine one or more of these more valuable products.

The adjusted syngas, comprising the second syngas and a hydrogen containing stream, may be formed in situ in the second Fischer-Tropsch reactor. In such a case, both

the second syngas and the hydrogen containing stream would be fed directly to the second Fischer-Tropsch reactor.

According to the present invention, the third syngas comprises a reduced amount of CO₂ than was present in the adjusted syngas, meaning that the adjusted syngas has a greater total amount or quantity of CO₂ than does the third syngas. Therefore, although the percent concentration of CO₂ in the third syngas may be greater than the percent concentration of CO₂ in the adjusted syngas, the third syngas comprises a reduced total amount or quantity of CO₂.

The blender that blends the hydrocarbonaceous products should be understood to include any suitable means for blending including, but not limited to, mixers, blenders, agitators and stirrers, including, for example, those described in Section 18 of Perry's Chemical Engineer's Handbook, Seventh Edition; (1997), the disclosure of which is hereby incorporated by reference in its entirety. Blending can be accomplished in a variety of ways commonly known to those of skill in the art. By way of example, blending may be accomplished by sending the products to a common distillation unit or separator, as shown in the preferred embodiment described below. In such a case, the common distillation unit or separator would serve as the blender.

The H₂-containing stream can be mixed with the second syngas at least one of before, during or after entering the second Fischer-Tropsch reactor. The H₂-containing stream can be recovered from any number of sources in the Fischer-Tropsch process. Suitable sources of a H₂-containing stream include, but are not limited to, syngas, unreacted gas streams from the syngas conversion unit, gas streams associated with a hydrotreater/hydrocracker used for upgrading the product, gas streams associated with a reformer used to make an aromatic product, steam reforming of CH₄, combinations thereof and the like. With regard to steam reforming of CH₄ as a source of a H₂-containing stream, a steam reforming reactor may be needed to produce a H₂-containing stream for upgrading of C₁₀₊ product, via hydrotreating and hydrocracking. The H₂-containing stream can be recovered using any suitable recovery process including, but not limited to, adsorption,

absorption, cryogenic separation, membrane separation, combinations thereof and the like.

Additionally, while it is preferable to use recovered hydrogen, it is also acceptable to supplement or replace recovered hydrogen with hydrogen obtained from alternative sources. CO₂ is a by-product of steam reforming. Since this H₂-containing steam will be reacted with CO₂ from other sources, it is not essential that the CO₂ (or CO) be removed from it prior to reaction. If CO₂ and CO removal are needed from the portion of the H₂ intended for upgrading of the C₁₀₊ product, this recovered CO₂ and CO can be reacted along with the other sources of CO₂.

In the processes of the present invention, suitable Fischer-Tropsch reactors include, but are not limited to, slurry bed reactors, fixed bed reactors, fluidized bed reactors, combinations thereof and the like. The first Fischer-Tropsch reactor is preferably a slurry bed reactor that contains a Co catalyst. Additionally, process conditions during operation of the first Fischer-Tropsch reactor and the catalyst used therein are preferably selected so that the water gas shift reaction occurring therein is not promoted to an appreciable extent.

A feature of the second Fischer-Tropsch reactor is that it is capable of converting CO₂. Catalysts that do so are called Shifting Fischer-Tropsch catalysts. Preferably, the second Fischer-Tropsch reactor contains an iron catalyst. In the second Fischer-Tropsch reactor CO₂ is converted into additional hydrocarbonaceous product and a second unreacted syngas having a reduced CO₂ content. The H₂-containing stream added to both the first and second Fischer-Tropsch reactors should contain essentially no sulfur, as both cobalt-catalyzed and iron-catalyzed Fischer-Tropsch catalysts are readily poisoned by sulfur, and >50% H₂, but may contain impurities such as hydrocarbons, inert gases, N₂, and light alcohols.

In addition to minimizing CO₂ emissions, the processes of the present invention also provide more efficient conversion of syngas into valuable hydrocarbonaceous products. Sources of syngas suitable for the present invention, include, but are not limited to, CH₄, coal, hydrocarbonaceous products, combinations thereof and the like. Syngas can be derived from a combination of these sources by using syngas generators.

Suitable syngas generators, according to the present invention, can include a light hydrocarbon reformer or a heavy hydrocarbon reformer. Light hydrocarbon reformers can employ a variety of technologies including, but not limited to, steam reforming, partial oxidation, dry reforming, series reforming, convective reforming, autothermal reforming, combinations thereof and the like. Generally, light hydrocarbon reformers change the mixture of hydrocarbon products in a hydrocarbon product mixture. Regardless of the specific technology used, syngas will be produced from CH_4 and an oxidant such as, for example, O_2 , CO_2 , air, enriched air, combinations thereof and the like. The resulting gas product typically contains some CO_2 and steam, in addition to syngas.

Series reforming, convective reforming and autothermal reforming incorporate more than one syngas-forming reaction in order to better utilize the heat of reaction. The above processes for producing syngas or obtaining syngas from C_1 - C_3 alkanes are well known in the art. Steam reformation is typically performed by contacting C_1 - C_3 alkanes with steam, preferably in the presence of a reforming catalyst, at a temperature of about 1,300°F (about 705°C) to about 1,675°F (about 913°C) and a pressure of about 10 psia (about 0.7 bars) to about 500 psia (about 34 bars). Suitable reforming catalysts include, for example, nickel, palladium, nickel-palladium alloys, combinations thereof and the like.

Regardless of the system used to produce syngas, it is desirable to remove any sulfur compounds such as, for example, hydrogen sulfide and mercaptans, contained in the C_1 - C_3 alkane feed. The removal of sulfur compounds can be achieved, for example, by passing the C_1 - C_3 alkane gas through a packed bed sulfur scrubber containing a zinc oxide bed or other slightly basic packing material. If the amount of C_1 - C_3 alkanes exceeds the capacity of the syngas unit, surplus C_1 - C_3 alkanes can be used to provide energy throughout the facility. For example, excess C_1 - C_3 alkanes can be burned in an upstream boiler to provide steam used in a thermal cracking step in the process of the present invention.

A heavy hydrocarbon reformer converts coal, heavy petroleum stocks or combinations thereof into syngas. The temperature in the reaction zone of the syngas generator is in the range of about 1,800°F to about 3,000°F and the pressure is in the range

of about 1 atm to about 250 atm. The atomic ratio of free oxygen in the oxidant to carbon in the feedstock (i.e., O/C, on an atom to atom basis) is preferably in the range of about 0.6 to about 1.5 such as, for example, about 0.80 to about 1.3. The free oxygen containing gas or oxidant is selected from the group consisting of air, O₂-enriched air (i.e., about 21 mol% to about 95 mol% O₂) and substantially pure O₂ (i.e., at least about 95 mol% O₂). An effluent gas stream leaving the partial oxidation gas generator has the following composition in mol%, depending on the amount and composition of the feed streams: about 8.0 to about 60.0 H₂, about 8.0 to about 70.0 CO, about 1.0 to about 50.0 CO₂, about 2.0 to about 75.0 H₂O, about 0.0 to about 30.0 CH₄, about 0.1 to about 2.0 H₂S, about 0.05 to about 1.0 COS, about 0.0 to about 8.0 N₂ and about 0.0 to about 2.0 Ar. Entrained in the effluent gas stream is particulate matter comprising about 0.5 wt% to about 30 wt% particulate carbon, preferably about 1 wt% to about 10 wt% particulate carbon (based on the weight of carbon in the feed to the gas generator). Fly ash particulate matter can be present along with the particulate carbon and molten slag. Conventional gas cleaning and/or purification steps can also be employed. See, for example, U.S. Patent No. 5,423,894 to Texaco, incorporated herein by reference in its entirety.

It should be recognized that CO₂ recycled to the first Fischer-Tropsch reactor serves a useful purpose. That is, CO₂ recycled to the first Fischer-Tropsch reactor serves as a diluent for reactive syngas components such as, for example, H₂ and CO. Inert CO₂ acts to dissipate heat generated during operation and can improve process control. As CO₂ is consumed by the second Fischer-Tropsch reactor, other inert gas components build up in the recycled gas. These inert components can include methane, N₂, Ar and other inert gas elements. Methane components can originate from unconverted methane in the syngas generator and methane formation that occurs in the first Fischer-Tropsch reactor. The N₂, Ar and other inert gas elements can be generated from an air separation unit or may also be obtained from an original natural gas feedstock. Normally, CO₂ is the most abundant inert gas component. However, when CO₂ is removed, in accordance with processes of the present invention, the concentration of other inert gas components can increase. These other inert gas components can act as a substitute for the removed CO₂ to improve

management of heat released in the first Fischer-Tropsch reactor. As a result, more of the carbon (as carbon monoxide) in the recycled gas can be processed. The increased processing of carbon (as carbon monoxide) improves overall carbon efficiency as does the direct conversion of CO₂ to products in the second Fischer-Tropsch reactor. Carbon efficiency is defined as the ratio of C₃₊ products to feed methane in the process. However, because of the increased concentration of other inert gas components, it may eventually be necessary to purge the other inert gas components from the system to be used in other applications, thereby producing a methane-enriched gas. In normal operation, the purged gas is rich in CO₂ and has a low heating value making its use limited. However, according to the present invention, the purged gas will be depleted in CO₂ and enriched in other gases, typically methane, thus increasing its heating value and uses.

In the recycling gas operation, the composition of the blended syngas, introduced to the first Fischer-Tropsch reactor, will change as the second Fischer-Tropsch reactor converts CO₂ into other products. That is, the concentration of other inert gas components will increase, and the concentration of reactive syngas components will remain essentially constant. As previously explained, the blended syngas is a combination of the first syngas, from the syngas generator, and the third syngas, that is recycled to the first Fischer-Tropsch reactor. The following table provides typical ranges of syngas compositions for a process that generates syngas from an O₂ source of about 99.5% purity.

Component, mol%	Typical FT Unit without CO ₂ conversion	With low level of CO ₂ conversion	With moderate level of CO ₂ conversion	With high level of CO ₂ conversion
H ₂	30	30	30	30
CO	40	40	40	40
CO ₂	20	15	10	5
N ₂ +Ar	2	3	4	6
C ₁ +Hydrocarbons	8	12	16	19

It should be recognized that not all of the syngas from the first reactor needs to be processed in the second reactor. Because CO₂, as an inert, builds up slowly and reasonable concentrations of CO₂ can be tolerated (e.g., about 60 mol%), only a portion of the syngas from the first reactor needs to be processed in the second reactor to achieve a desired CO₂ conversion. Accordingly, the size of the second Fischer-Tropsch reactor can be relatively small.

In certain circumstances, it is undesirable to process syngas from the first Fischer-Tropsch reactor and then recycle the CO₂-depleted syngas back to the first reactor. It has been surprisingly discovered that a reduction in CO₂ emissions can also be achieved by using a portion of the unreacted syngas from a first Fischer-Tropsch reactor as a feed to a second Fischer-Tropsch reactor.

Water is a natural product of the Fischer-Tropsch and synthesis gas generation reactions. Preferably, water generated from both the first and second reactors and the syngas generator is separated from the syngas products and the hydrocarbonaceous products. If not removed, the water can promote undesirable reverse water gas shift reactions that can convert CO into additional CO₂.

A preferred embodiment of the present invention is depicted in Figure 2. In this embodiment, a feedstream 10 comprising CH_4 , O_2 , H_2O , and optionally CO_2 enters a syngas generator 12. The syngas generator 12 generates water 13 and a first syngas stream 14. The syngas formed in the syngas generator 12 is cooled, and water 13 is removed after being condensed. Additionally, the first syngas stream 14 exits the syngas generator 12 and enters a first Fischer-Tropsch reactor 16, which generates stream 17 comprising a second syngas and a first hydrocarbonaceous product along with water.

Stream 17, containing the second syngas, exits the first Fischer-Tropsch reactor 16 and enters a first separator 18, which separates an unreacted by-product stream 19, a water stream 20 and a hydrocarbonaceous stream 21, comprising C_{5+} liquids. The water stream 20 exits the first separator 18. A portion of the unreacted gas stream 19 enters a second Fischer-Tropsch reactor 30. Separator 18 is a generalized representation of the product separation, representing one or more separation zones, some of which may be internal to the Fischer-Tropsch reactor, and some of which may be external to the Fischer-Tropsch reactor.

A second Fischer-Tropsch synthesis is conducted in the second Fischer-Tropsch reactor 30 generating stream 31 comprising a third syngas and a second hydrocarbonaceous product along with water. Stream 31, containing the third syngas, exits the second Fischer-Tropsch reactor 30 and is recycled to the first separator 18. The hydrocarbonaceous product stream 21 exits the first separator 18 and enters a second separator 22. The second separator 22 separates the hydrocarbonaceous product stream 21 into a product stream 23 comprising $\text{C}_1\text{-C}_5$, having a H:C ratio of about 2.0, a product stream 24 and a C_{10+} product stream 25, having a H:C ratio of about 2.0.

The product stream 24 exits the second separator 22 and enters a naphtha reformer 26. The naphtha reformer 26 upgrades the product stream 24 to produce a $\text{C}_6\text{-C}_{10}$ product stream 27, having a H:C ratio below about 2.0. The naphtha reformer 26 also generates a H_2 -containing stream that exits the naphtha reformer 26 in a stream 28 that is recycled to be mixed with the unreacted gas stream 19, exiting the first separator 18, prior to entering

the second Fischer-Tropsch reactor 30. The stream 28 mixes with the unreacted gas stream 19 so that a mixture comprising both unreacted gas, from the first separator 18, and a H₂-containing stream, from the reformer 26, enters the second Fischer-Tropsch reactor 30 in a mixed stream 29. Thus, mixed stream 29 is the adjusted syngas mentioned earlier.

5 Additionally, a portion of the unreacted gas stream 19, exiting the first separator 18, can be divided into two additional streams. The first stream can be comprised of excess unreacted gas comprising CO, H₂ and CO₂. This stream exits the process in an exit stream 32, to be used as fuel. The second stream can be recycled in a stream 33 to be mixed with the feed gas 10, producing a mixed feed gas 11 that enters the syngas generator 12. At least a portion of the third syngas in the second product stream 31 is directed in a stream 35 to be blended with the first syngas stream 14, producing a blended syngas stream 15. Additionally, another portion of the unreacted gas stream 19 is recycled in a syngas recycle stream 33. The syngas recycle stream 33, mixes with the feed gas stream 10 producing a mixed feed gas stream 11 that enters the syngas generator 12. Also, a portion of the syngas recycle stream 33 can be directed in a stream 34 that mixes with the blended syngas stream 15, producing a mixed syngas stream 36 that is introduced into the Fischer-Tropsch reactor 16. Although the embodiment depicted in Fig. 2 comprises two Fischer-Tropsch reactors, additional reactors can be used as desired. For instance, additional reactors may be used in instances where even greater CO₂ reduction is desired.

Generally, the operating conditions for the second Fischer-Tropsch reactor used to convert CO₂ should be:

Variable	Broad	Preferred
Pressure, Atmospheres	1-20	10-18
Temperature, °C	250-425	300-360
CO+CO ₂ conversion, %	10-70	30-50
H ₂ :(CO+CO ₂) ratio	1-8	1.25-3

5

EXAMPLE

In initial operation of the following example, a first syngas is fed to a first Fischer-Tropsch reactor. A second syngas is recovered from the Fischer-Tropsch reactor and fed to a second Fischer-Tropsch reactor. A third syngas is recovered from the second Fischer-Tropsch reactor. This third syngas may then be blended with the first syngas to form a blended syngas, which would be fed into the first Fischer-Tropsch reactor.

A first synthesis gas is formed from CH₄ by reactions that include partial oxidation in a syngas generator. The O₂ used in the first syngas formation has a purity of about 99.5 vol%. The first syngas from the reactor contains about 5 vol% CO₂. Water produced in the syngas generator is separated from other components and is disposed of. The first syngas is blended with a third syngas, forming a blended syngas. The blended syngas has a CO₂ content of about 10 vol%, and the blended syngas is processed in a first Fischer-Tropsch reactor that uses a Co-containing catalyst in a slurry bed-type reactor. The unreacted syngas (i.e., the second syngas), contained in the products from the first Fischer-Tropsch reactor has a higher CO₂ content, when expressed on the basis of C₃ and lower molecular weight species including inerts, than was present in the blended syngas.

The gas and liquid products from the first Fischer-Tropsch reactor are sent to a separation complex comprised of API separators, distillation columns and other standard

equipment items. With a slurry bed reactor, effluent leaves the reactor in two or more streams, wherein at least one stream is a vapor stream and one stream is a liquid stream. The vapor stream leaving the first Fischer-Tropsch reactor contains the second syngas. The streams from the separation complex are comprised of water, hydrocarbonaceous products and unreacted syngas. Since a separation complex is needed for the products from the first and second syngas reactors, it is economically desirable to use a single separation complex for both reactors.

A portion of the syngas from the separator, that contains the second syngas along with some of the third syngas, is mixed with a H₂-containing stream, produced later in the process, to produce an adjusted syngas with a H₂:(CO+CO₂) ratio of about 2.0. The portion of the syngas from the separator is processed in a second Fischer-Tropsch reactor. The third syngas contained in the products from the second Fischer-Tropsch reactor comprises a reduced amount of CO₂, when expressed on the basis of CO, H₂ and CO₂, than was present in the syngas feed to the second Fischer-Tropsch reactor. In the second Fischer-Tropsch reactor, the CO₂ conversion is about 40%, the temperature is about 320°C and the pressure is about 10 atmospheres.

The effluent from the second Fischer-Tropsch reactor is sent to the separation complex. The hydrocarbonaceous product from the separation complex is then further separated to provide a C₅ product, a C₆-C₁₀ containing product and a C₁₀+ containing product. The C₁₀+ containing product is converted into products that include, but are not limited to, diesel fuel having a H:C molar ratio of about 2.0 or greater. The C₆-C₁₀ containing product can be reformed to produce an aromatic product having a H:C molar ratio of below about 2.0 and H₂. The H₂-containing stream produced during reformation is recycled to the second Fischer-Tropsch reactor where it is used to convert the CO₂.

An additional portion of the syngas from the separation complex, containing the second syngas and third syngas, is mixed with the first syngas from the syngas generator, forming a blended syngas. The blended syngas is then processed in the first Fischer-Tropsch reactor.

While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those of ordinary skill in the art without departing from the spirit and scope of the appended claims.